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### Title

Assessing methods to estimate emissions of non-methane organic compounds from landfills.

### Permalink

<https://escholarship.org/uc/item/5722209m>

### Journal

Waste management (New York, N.Y.), 34(11)

### ISSN

0956-053X

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### Publication Date

2014-11-01

### DOI

10.1016/j.wasman.2014.07.007

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Peer reviewed



## Assessing methods to estimate emissions of non-methane organic compounds from landfills



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### ARTICLE INFO

#### Article history:

Received 7 January 2014

Accepted 13 July 2014

Available online 6 August 2014

#### Keywords:

NMOC emission

NMOC flux estimation

Field measurement

Landfill gas emission

### ABSTRACT

The non-methane organic compound (NMOC) emission rate is used to assess compliance with landfill gas emission regulations by the United States Environmental Protection Agency (USEPA). A recent USEPA Report (EPA/600/R-11/033) employed a ratio method to estimate speciated NMOC emissions (i.e., individual NMOC emissions): speciated NMOC emissions = measured methane ( $\text{CH}_4$ ) emission multiplied by the ratio of individual NMOCs concentration relative to  $\text{CH}_4$  concentration ( $C_{\text{NMOCs}}/C_{\text{CH}_4}$ ) in the landfill header gas. The objectives of this study were to (1) evaluate the efficacy of the ratio method in estimating speciated NMOC flux from landfills; (2) determine for what types of landfills the ratio method may be in error and why, using recent field data to quantify the spatial variation of ( $C_{\text{NMOCs}}/C_{\text{CH}_4}$ ) in landfills; and (3) formulate alternative models for estimating NMOC emissions from landfills for cases in which the ratio method results in biased estimates. This study focuses on emissions through landfill covers measured with flux chambers and evaluates the utility of the ratio method for estimating NMOC emission through this pathway. Evaluation of the ratio method was performed using  $\text{CH}_4$  and speciated NMOC concentration and flux data from 2012/2013 field sampling of four landfills, an unpublished landfill study, and literature data from three landfills. The ratio method worked well for landfills with thin covers (<40 cm), predicting composite NMOC flux (as hexane-C) to within a factor of  $10\times$  for 13 out of 15 measurements. However, for thick covers ( $\geq 40$  cm) the ratio method overestimated NMOC emissions by  $\geq 10\times$  for 8 out of 10 measurements. Alternative models were explored incorporating other chemical properties into the ratio method. A molecular weight squared ( $\text{MW}^2$ )-modified ratio equation was shown to best address the tendency of the current ratio method to overestimate NMOC fluxes for thick covers. While these analyses were only performed using NMOC fluxes through landfill covers measured with flux chambers, results indicate the current USEPA approach for estimating NMOC emissions may overestimate speciated NMOC emission  $\geq 10\times$  for many compounds.

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### 1. Introduction

With 54–69% of municipal solid waste (MSW) discarded in landfills in 2008, landfill disposal remains a major waste management option in the United States (USEPA, 2010; van Haaren et al.,

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2010). The decomposition of MSW organics in landfills produces landfill gas (LFG) that contains methane (55–60 vol%), carbon dioxide (40–45 vol%), and traces of non-methane organic compounds (NMOCs) at pptv to ppmv levels including alkanes, alkenes, aromatics, chlorinated ethylenes, chlorinated methanes, halocarbons, alcohols, ketones, terpenes, chlorofluoro compounds (CFCs), and siloxanes (Staley et al., 2006; Brosseau and Heitz, 1994). Gas control at MSW landfills is regulated in the United States under the Clean Air Act (section 111) New Source Performance Standards (NSPS)/Emission Guidelines (EG) (40 CFR part 60) (USEPA, 1996). Landfills with design capacity of  $\geq 2.5$  million Mg (or million cubic

meters) or annual NMOC emissions >50 Mg are required to install gas control and collection systems. Thus, estimates of annual NMOC emissions are important for compliance with environmental regulations. While there are established techniques for measuring a whole-landfill CH<sub>4</sub> emission rate (i.e., tracer dilution method (Czepiel et al., 1996) and inverse plume modeling (Babilotte et al., 2010)), no such methods exist for measuring a whole-landfill NMOC emission rate. Instead, methods for estimating NMOC emission rate are employed.

Under the NSPS/EG, landfills may estimate their annual NMOC “emission” rate using a three tier approach. In the Tier 1 approach, the NMOC emission rate is estimated using

$$M_{NMOC} = \sum_{i=1}^n 2kL_0M_i(e^{-kt_i})C_{NMOC}3.6 \times 10^{-9} \quad (1)$$

where  $M_{NMOC}$  is the mass emission rate of NMOC from the landfill (Mg/yr),  $k$  is the CH<sub>4</sub> generation rate constant (year<sup>-1</sup>),  $L_0$  is the CH<sub>4</sub> generation potential (m<sup>3</sup>/Mg of solid waste),  $M_i$  is the mass of solid waste in the  $i$ th section (Mg),  $t_i$  is age of the solid waste in the  $i$ th section (yr),  $C_{NMOC}$  is concentration of NMOC in the LFG (ppmv as hexane-C),  $n$  is the number of sections into which the landfill is divided, and  $3.6 \times 10^{-9}$  is a units conversion factor. For the Tier 1 approach, default values are specified for the model parameters in Eq. (1):  $k = 0.05$  yr<sup>-1</sup> (or  $0.02$  yr<sup>-1</sup> in arid regions),  $L_0 = 170$  m<sup>3</sup> of CH<sub>4</sub>/Mg of solid waste, and  $C_{NMOC} = 4000$  ppmv when no field measurements are available. The term “emission” as used by USEPA to describe  $M_{NMOC}$  computed from Eq. (1) is somewhat misleading, since Eq. (1) is an expression for gas production. Some fraction of the gas is collected, some is oxidized in the cover soil, and some is emitted and is referred to as a fugitive emission. With this approach, the NMOC emission rate is the product of the total LFG production rate and a fixed concentration of NMOC in the landfill gas. In the Tier 2 approach, measured site-specific NMOC concentrations in LFG are determined using USEPA Method 25, 25C or 18 and are substituted for the 4000 ppmv assumed in Eq. (1), where NMOC concentrations of individual species are first expressed as  $C_{NMOC}$  as carbon and then divided by six to estimate  $C_{NMOC}$  as hexane. Under the Tier 3 approach, a site-specific estimate of the CH<sub>4</sub> generation constant,  $k$ , in Eq. (1) is obtained by USEPA Method 2E in addition to the site-specific NMOC concentrations to calculate the annual NMOC emission rate.

Consistent with the NSPS/EG Tier 2 and Tier 3 approaches, a recent USEPA Report (EPA/600/R-11/033) (USEPA, 2012) estimated the NMOC emission rates based on CH<sub>4</sub> emission measurements and landfill header gas measurements of individual NMOCs using

$$Q_{NMOCs} = Q_{CH_4} \frac{C_{NMOCs}}{C_{CH_4}} \frac{\dot{M}_{NMOCs}}{\dot{M}_{CH_4}} \quad (2)$$

where  $Q_{NMOCs}$  is the emission rate of an individual NMOCs (MT<sup>-1</sup>),  $Q_{CH_4}$  is the measured CH<sub>4</sub> emission rate (MT<sup>-1</sup>),  $C_{NMOCs}$  is the concentration of an individual NMOCs in the header gas (ppm by volume),  $C_{CH_4}$  is the concentration of CH<sub>4</sub> in the header gas (ppm by volume), and  $\dot{M}_{NMOCs}$  and  $\dot{M}_{CH_4}$  are the molecular weights of the individual NMOCs and CH<sub>4</sub>, respectively. Eq. (2) is similar to the ratio approach used in many studies employing a tracer gas to measure whole-landfill CH<sub>4</sub> emissions (Scheutz et al., 2011; Czepiel et al., 1996; Lamb et al., 1995). The use of molecular weight (MW) ratio is to make the units consistent to mass flux (MT<sup>-1</sup>) when concentrations are given in ppm by volume. As used in those tracer studies, the following conditions must be met for Eq. (2) to hold: (1) the transport and dispersion properties of CH<sub>4</sub> and tracer gas are the same over the distance and time scales considered, and (2) any chemical loss and deposition must be similar over the distance and time scales under consideration (Scholtens et al., 2004). In Eq. (2), CH<sub>4</sub> serves as the “tracer gas” for individual NMOCs.

While calculations of NMOC collection using measured gas flow rates and concentrations are straightforward, estimation of NMOC emissions in the uncollected gas (i.e., fugitive emissions) using Eq. (2) is more complex and subject to uncertainty. The objectives of this study were to (1) evaluate the efficacy of the ratio method (Eq. (2)) in estimating speciated NMOC flux from landfills; (2) determine for what types of landfills the ratio method may be in error and why, using recent field data to quantify the spatial variation of ( $C_{NMOCs}/C_{CH_4}$ ) within landfills; and (3) formulate alternative models for estimating NMOC emissions from landfills for cases in which the ratio method results in biased estimates. Ideally, these objectives could be met by examining whole-landfill NMOC emissions, e.g., through an integrative method like the tracer dilution method (Czepiel et al., 1996). Because NMOC emission rate measurements were only available through landfill covers with flux chamber measurements, these more limited data were used in this assessment.

## 2. Evaluation approach

The ratio method of estimating NMOC flux (Eq. (2)) assumes that the concentrations of individual NMOCs relative to CH<sub>4</sub> in the header gas are representative of their concentrations in LFG that escapes into the atmosphere. To quantify spatial variation of NMOCs/CH<sub>4</sub> concentration ratios ( $C_{NMOCs}/C_{CH_4}$ ) in landfills, LFG samples for CH<sub>4</sub> and NMOC analyses were collected in 2012/2013 from four landfills (Southeastern-US; Midwestern-US 1; Midwestern-US 2; Yolo County, CA) at various locations (header gas, vent pipe, above ground at landfill surface near active landfill face, and in gas-filled landfill pores away from gas collection wells). A description of these landfill sites including landfill cover types and thickness, sampling dates, and environmental conditions during sampling is provided in Table 1.

Pore gases in these landfills were collected using stainless steel or Teflon tubing that were installed using geoprobes at desired depths (0.3–2.4 m). Tubing was purged and gas samples of 25–50 mL for major gases (CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>) were withdrawn with a syringe and stored in pre-evacuated glass serum bottles. All major gases were analyzed at Florida State University. Gas samples with CH<sub>4</sub> and CO<sub>2</sub> concentrations below 1% v/v were determined on a Shimadzu 14A gas chromatograph with a flame ionization detector and a methanizer, a 1 mL sampling loop, and a 2-m 0.32 cm diameter stainless steel column packed with Carbosphere. Methane and CO<sub>2</sub> concentrations above 1% v/v, N<sub>2</sub>, and O<sub>2</sub> + Ar were determined on a Shimadzu 8A gas chromatograph with a thermal conductivity detector. For speciated NMOCs, gas samples were collected in 2 L stainless steel canisters and analyzed by the Blake–Rowland Laboratory at the University of California–Irvine, the same laboratory used for NMOC analyses in Scheutz et al. (2003, 2008) data sets. NMOC analyses were conducted using two separate high resolution analysis systems consisting of multi-column/detector GC (gas chromatography) and combined GC/MS (mass spectrometry). Measured concentrations of individual NMOCs and methane were used to determine speciated  $C_{NMOCs}/C_{CH_4}$  ratios.

In addition to the field sampling data, CH<sub>4</sub> and speciated NMOC flux data from three published papers (Scheutz et al., 2003; Barlaz et al., 2004; Scheutz et al., 2008) and an unpublished 2005 study at Leon County landfill, FL (Chanton, 2013) were reviewed and processed. These data sets have a total of 37 landfill surface locations (i.e., 37 separate measurement points on landfill surfaces) wherein emission rates of 35–53 speciated NMOCs and CH<sub>4</sub> were measured using static flux chambers. As shown in Table 2, the data were collected from point locations of different landfill cover systems (i.e., soil types, biocover, cover thickness), under prevailing environ-

**Table 1**

Characteristics of landfill sites in 2012/2013 field sampling.

Landfill	Active gas collection system	LF cover systems		Environmental observations			Sampling dates	No. of samples	No. of NMOCs detected
		Thickness (cm)	Components	Ambient temperature (°C)	Soil temperature (°C)	Soil moisture <sup>a</sup>			
Southeastern-US	No	30	Intermediate cover, light vegetation	23–24	26–29	dry	April 26, 2012	8	81
				35.4–41.2	31.1–49.7	dry	June 28, 2012	8	81
Midwestern-US 1	No	30	Intermediate cover, hard soil, no vegetation	32.8–38.2		dry	July 12, 2012	12	81
Midwestern-US 2	Yes	15	Clay soil layer	26.6	26.1	very wet	August 28–30, 2012	22	79
							September 10, 2012	5	79
Yolo County, CA	Yes	50–60	Intermediate cover, clay soil with light vegetative			dry	September 21, 2012	14	79

<sup>a</sup> Based on visual observations (Fig. S2).**Table 2**

Characteristics of previous landfill study sites (data sets).

Landfill	Refuse age (yrs)	Active gas collection system	LF cover systems		Environmental conditions		No. of locations tested <sup>a</sup>	CH <sub>4</sub> flux (g m <sup>-2</sup> d <sup>-1</sup> ) <sup>b</sup>		% CH <sub>4</sub> oxidation
			Thickness (cm)	Components	Ambient temperature (°C)	Cover moisture content % wet wt		Range	Mean	
Grand'Landes (GL), France (Scheutz et al., 2008)	~12	Yes	100	30 cm Vegetative soil layer + 70 cm compacted clay liner + embankment of soil & waste	13–27	13–19 With max at 25 cm	6	–1.1E–3 to 29.0	9.1	25–35
Lapouyade (LP), France (Scheutz et al., 2003)	3–5	Yes	120	Fully vegetated surface + 80 cm loam + 40 cm of coarse sand	9.7–25.3	<6.5 At 5–35 cm; 10.7–12.7 at 45–120 cm	4	–9.5E–4 to 10.0	2.5	40 ± 7 <sup>c</sup>
			40	40 cm Of coarse sand layer			1		49.9	3.8 ± 1.3
Outer Loop (OL), KY (Barlaz et al., 2004)	3–5	Yes	100	~ 100 cm Clay soil layer	26.3 ± 6.4	14.6	2	–0.11 to –0.14 (June'02)	–0.13	21
					15.4–28.9	22.5	1		0.32 (June'03)	
			130	100 cm Compost + 15 cm tire chips + 15 cm clay soil	26.3 ± 6.4	53.1	2	8.54–9.24 <sup>d</sup> (June'02)	8.9	54
					15.4–28.9	63.0	1		0.02 (June'03)	
							3	–1.8E–1 to –1.4E–1	–0.15 (June'02)	
Leon County (LC), FL (Chanton's data)	~2	No	15	Clay soil layer	36.7–43.0		4	1.9 to 78.2 (May'05)	35.6	32–87
							4	13.4 to 165.9 (November'05)	77.5	
			30	15 cm Mulch + 15 cm clay soil layer	25.7–39.9		4	2.2E–2 to 4.7 (May'05)	1.9	0–76
							4	–0.25 to 5.6 (November'05)	1.6	

<sup>a</sup> Static chamber tests for both CH<sub>4</sub> and NMOCs fluxes.<sup>b</sup> g m<sup>-2</sup> d<sup>-1</sup> (grams per square meter per day).<sup>c</sup> ±Values represent one standard deviation.<sup>d</sup> CH<sub>4</sub> flux came from water clogged compost.

mental conditions (ambient temperature, soil moisture content), and CH<sub>4</sub> flux range (hotspot, lowspot). Additional data on concentrations of CH<sub>4</sub> and speciated NMOCs at the landfill surface, within the soil profile, and in header gas or vent pipes that were measured in these studies but not provided in the previous publications were obtained from the corresponding authors. The measured CH<sub>4</sub> and speciated NMOCs concentrations at the landfill surfaces were determined using the first gas sample collected in flux chamber measurements made at each site. While atmospheric pressure data

were collected during some of these studies, e.g., Barlaz et al. (2004), knowledge of both atmospheric pressure and internal landfill gas pressure immediately beneath the landfill cover is necessary to estimate the driving force for advective gas transport through landfill covers (Jung et al., 2011). Unfortunately, these data were unavailable.

A spreadsheet database containing 71 reported NMOCs from these four data sets was developed. Various chemical properties (molecular structure, molecular weight (MW), molar volume,

Henry Law's constant ( $k_H$ ), aqueous solubility ( $S_w$ ), log octanol–water partition coefficient ( $\log K_{ow}$ ), vapor pressure (VP) and probability of biodegradability were collected from existing chemical databases (NIST Chemistry WebBook and USEPA's Estimation Program Interface (EPI) Suite TM v. 4.1) and incorporated into the NMOC database developed for this project. The NMOC data sets were also categorized into various chemical groups including alkanes, alkenes, aromatics, chlorinated ethylenes, chlorinated methanes, halocarbons, polar nitrates, and bromides.

### 3. Results and discussion

#### 3.1. LFG concentrations from field sampling in 2012/2013

There were 79–81 NMOCs detected in landfill gas samples obtained from Southeastern-US, Midwestern-US 1, Midwestern-US 2, and Yolo County, CA landfills. Overall, 23 of 79–81 detected NMOCs had measured concentrations that were 1–3 orders of magnitude lower than the AP-42 (Compilation of Air Pollutant Emission Factors) uncontrolled default concentrations for estimating emissions from landfills when site-specific data are not available [Tables S1–S4 of the supporting information (SI)].

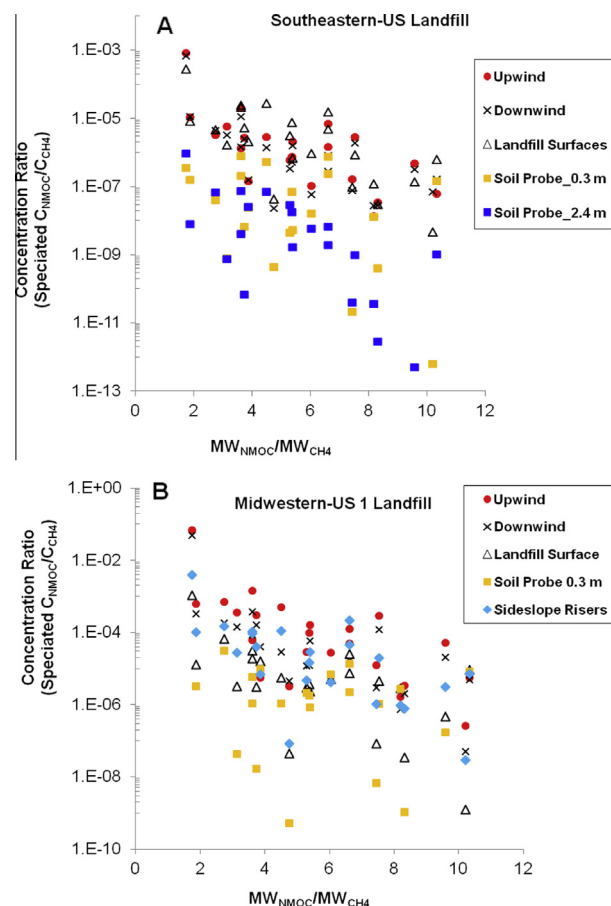
##### 3.1.1. Vertical variability in LFG concentrations

The concentration ratios of speciated NMOCs listed in AP-42 to  $\text{CH}_4$  are shown in Figs. 1 and 2A for Southeastern-US, Midwestern-US 1, and Yolo County landfills.  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios vary vertically with higher ratios in gas samples obtained at shallower depths relative to deeper depths. Compare, for example, landfill surface data with samples at 0.3 m depth in Fig. 1, and geoprobe samples at 0.3 and 1.5 m depths in Fig. 2A. Similar vertical variations are observed in concentration ratios of speciated non-AP-42 NMOCs to  $\text{CH}_4$  at Southeastern-US (Fig. S1): higher  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios are generally observed on the landfill surface versus samples with depth. In these samples the significantly higher  $\text{CH}_4$  concentrations at deeper depths reduced the concentration ratios of speciated NMOCs to  $\text{CH}_4$  below the landfill surface (>0.30 m depths). As gas neared the surface, some methane biodegradation occurred, resulting in higher ratios.

The gas data from Midwestern-US 2 landfill, however, do not show differences in the  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios between measurements at the landfill surface and 0.55 and 2.4 m depths (Fig. 2B). Here, ratios of  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  are independent of sampling depth. One plausible explanation is the presence of considerable moisture in pores, which affects transport and reaction processes through this soil cover. The soil cover was wet during testing with some portions fully water saturated due to heavy rainfall prior to field sampling (Fig. S2). Excess moisture favors preferential gas flow, reduces oxygen availability and therefore aerobic biodegradation, and may slow rates of biodegradation because of the longer diffusional paths from gas to microbes in water-logged soil. These are likely factors that diminished chemical and biological reactions in this cover soil, which then resulted in  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios that remained unchanged with depth at this landfill.

##### 3.1.2. Horizontal variability in LFG concentrations

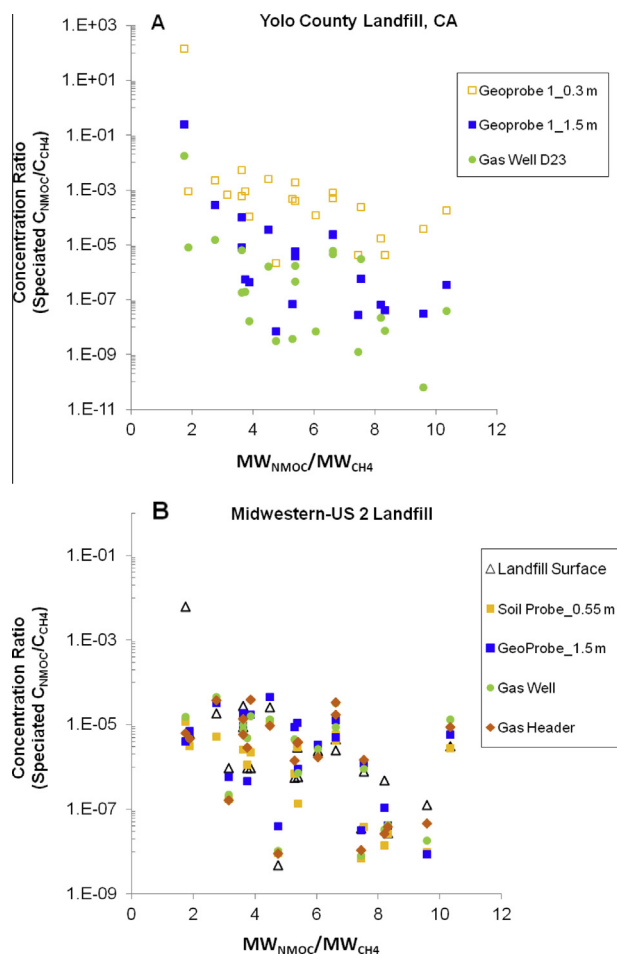
By using header gas data, the ratio method (Eq. (2)) assumes that  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the header gas represent analogous gas concentration ratios in surrounding wastes. At the Yolo County landfill, the  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in LFG samples taken from three geoprobe locations at 1.5 m depth (MW 1, MW 7, and MW 8, Fig. 3) and an adjacent extraction gas well are within a factor of 10 (Fig. 4A). For the probes closest to the well, using paired  $t$ -tests 58% and 53% of AP-42 speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in MW 1–1.5 m and MW 7–1.5 m, respectively, are statistically similar ( $p < 0.05$ ) to the speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the adjacent gas well.



**Fig. 1.** Vertical spatial variation of concentration ratios of speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  in (A) Southeastern-US and (B) Midwestern-US 1 landfills. Upwind and downwind refer to locations near the landfill: within ~1–2 km upwind or downwind of the landfill, based on wind direction during time of measurements. Both upwind and downwind gas plume samples were taken at 3 m above the ground surface. Data points represent the 23 identified AP-42 NMOCs in landfill gas samples.

Meanwhile, 95% of AP-42 speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in MW 8–1.5 m are statistically similar ( $p < 0.05$ ) to the speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the adjacent gas well. The speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in each probe that are significantly different from the speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios of the gas well at 95% confidence level are not systematically higher or lower than that of the gas well. Similarly, pore gas samples from three geoprobes at 1.5 m depth in Midwestern-US 2 landfill have comparable  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios with samples from gas well and gas header (Fig. 4B): 86% of speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the geoprobes are statistically similar ( $p < 0.05$ ) to the speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the gas well, and there is no systematic bias between the  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the geoprobes and the gas well. At least from these sites, Fig. 4 shows that off-gassing of some NMOCs due to vapor/vacuum interactions in the gas extraction process do not result in considerably higher NMOC concentrations in the gas well than in landfill pore gas surrounding the well. Therefore, header gas concentrations might reasonably represent  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the surrounding waste at these two landfills. However, header gas concentrations may be significantly different from gas concentrations in cover soil, at the landfill surface, and downwind of the landfill, since  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios vary significantly with depth from landfill surface to bottom of landfill cover (Figs. 1 and 2). The higher  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios near landfill surfaces observed in field sampling in 2012/2013 are consistent with similar elevated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios observed in landfill surface data from the literature data sets, which is discussed below.





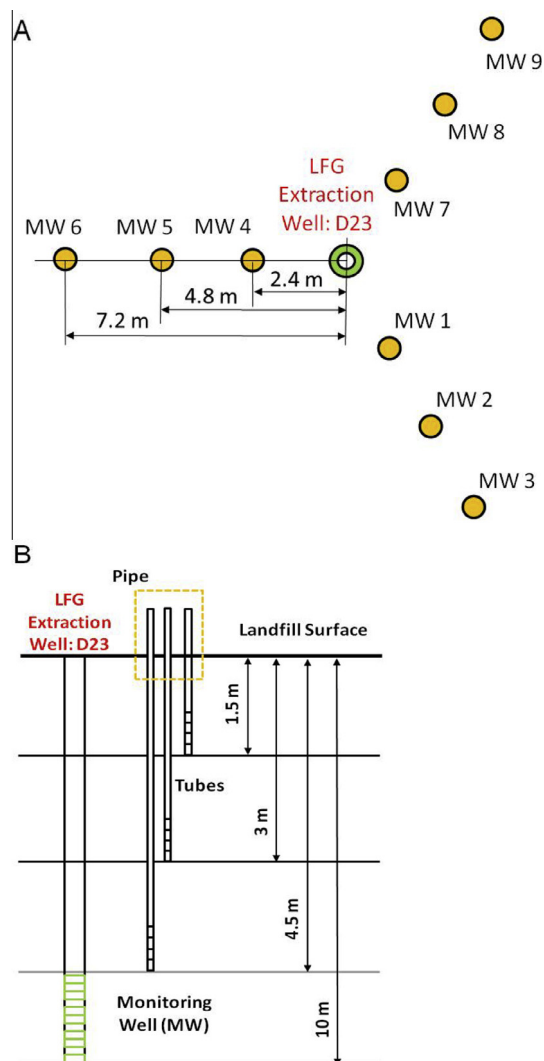
**Fig. 2.** Vertical spatial variation of concentration ratios of speciated  $C_{NMOCs}/C_{CH_4}$  in (A) Yolo County CA and (B) Midwestern-US 2 landfills. Data points represent the 23 identified AP-42 NMOCs in landfill gas samples.

### 3.2. NMOC fluxes and concentrations from literature

#### 3.2.1. Measured versus predicted speciated NMOC fluxes

Results using the ratio method to predict NMOC fluxes are summarized in Table 3 using data from four landfill sites studied in previous investigations (Scheutz et al., 2003, 2008; Barlaz et al., 2004; Chanton, 2013). The NMOC data sets are sorted according to type of landfill cover system, soil cover or biocover, thickness of the cover layer, and  $CH_4$  flux, positive or negative measured flux. Under these categories, the ratio method estimates are assessed by the percent of measured speciated NMOC data that are either overestimated or underestimated by  $\geq 10\times$  or within a factor of  $10\times$ . As noted in Table 2, soil covers may contain 1–2 layer of soils (e.g., sand, loam, clay, clay liner or vegetative soil) over a waste layer, while biocovers have 2–3 layers of media cover (i.e., mulch or compost layer + soil layer and possibly a highly permeable layer such as shredded tire chips) over refuse.

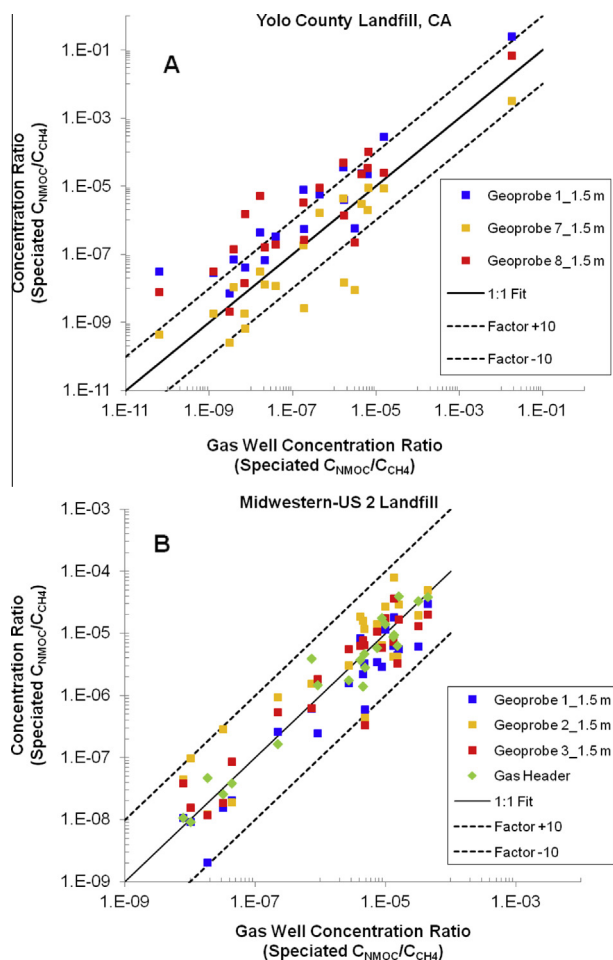
The ratio method does not work well for landfill covers  $\geq 40$  cm with positive  $CH_4$  fluxes. For soil covers with thickness 40–120 cm and  $CH_4$  flux  $0.3\text{--}49.9\text{ g m}^{-2}\text{ d}^{-1}$  (grams per square meter per day), 49–78% of speciated NMOC flux data are overestimated by a factor  $\geq 10\times$  (Table 3). In similarly thick biocovers where more biodegradation is expected, as much as 98% of speciated NMOC flux data are overestimated by a factor  $\geq 10\times$ . On average, 67% of the overestimated speciated NMOC fluxes in thick covers (soil or biocover) using the ratio method where positive  $CH_4$  fluxes occur have negative measured NMOC fluxes. The percent of ratio method



**Fig. 3.** Layout of sampling locations in one landfill cell at Yolo County Landfill, CA: (A) plan view and (B) elevation view.

overestimates that are due to negative measured NMOC fluxes tend to be greater in thick covers with low positive  $CH_4$  flux (Fig. S3B,  $CH_4$  flux =  $1.45\text{ g m}^{-2}\text{ d}^{-1}$ ) than in thick covers with high positive  $CH_4$  flux (Fig. S3A,  $CH_4$  flux =  $29.0\text{ g m}^{-2}\text{ d}^{-1}$ ).

Overestimation of NMOC fluxes with the ratio method might be explained by greater biodegradation of NMOCs than  $CH_4$  in landfill covers. Methane is often oxidized in landfill covers (Chanton et al., 2009, 2011) and significant potential for co-oxidation of NMOCs with methane has been demonstrated (Scheutz et al., 2003). However, this appears not to be the case for the majority of NMOCs where NMOC fluxes are overestimated. For example, 55% of NMOCs that are overestimated by a factor  $\geq 10\times$  in Grand'Landes data (Fig. S3A and B) are categorized as not ready biodegradable organic compounds based on aerobic biodegradation models (EPI Suite TM v. 4.1). The EPI Suite considers an organic compound to be ready biodegradable if its estimated ultimate biodegradation rate (i.e., complete conversion to  $CO_2$  and water) is in the order of weeks or faster (BIOWIN 3 model, semi-quantitative estimates) and with biodegradation probability  $>0.5$  (BIOWIN 5 model, fragment method developed using data on 884 chemicals from the Japanese MITI protocol). The molecular structures of the studied NMOCs are represented if not specifically included in the training and validation data sets for BIOWIN 3 and BIOWIN 5 models (Appendices F and G, BIOWIN User Guide, EPI Suite TM v. 4.1).



**Fig. 4.** Horizontal spatial variation of concentration ratios of speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  in (A) Yolo County and (B) Midwestern-US 2 landfills. Data points represent the 23 identified AP-42 NMOCs in landfill gas samples.

For thin landfill covers (15 cm clay soil), the ratio method works reasonably well with  $70 \pm 4\%$  of speciated NMOC flux data within a factor of  $10\times$  of ratio method estimates (Table 3). The data for thin landfill covers were collected from four landfill surface locations at the Leon County landfill (Chanton, 2013) that were tested for two periods: May '05 and November '05. In both tests, only  $20 \pm 5\%$  of NMOC flux data are overestimated by a factor  $\geq 10\times$  while  $11 \pm 6\%$  of NMOC flux data are underestimated by a factor  $\geq 10\times$ . Among the landfill study sites (Table 2), only Leon County landfill had no active gas collection system during the study period. As noted in Table 3, the range of positive  $\text{CH}_4$  flux in this data set ( $1.9\text{--}165.9 \text{ g m}^{-2} \text{ d}^{-1}$ ) is very wide. Except for some brominated compounds and chlorinated methanes, the ratio method works relatively well for various chemical groups of NMOCs in the thin soil covers at the Leon County landfill (Fig. S3C and D).

While the ratio method generally overestimates NMOC fluxes from thick covers, data in Table 3 show that this method underestimates NMOC emission rates when  $\text{CH}_4$  flux is considered zero for negative  $\text{CH}_4$  flux measurements (grey highlighted rows in Table 3). Here, negative  $\text{CH}_4$  flux is due to uptake of  $\text{CH}_4$  by oxidation in landfill covers. Two thick soil covers (Grand'Landes and Leon County landfills) and one thick biocover (Outer Loop landfill) have negative measured  $\text{CH}_4$  flux at some measurement locations, and 26–64% of NMOC flux measurements for these regions are underestimated by a factor  $\geq 10\times$  when  $\text{CH}_4$  flux is considered zero. While some NMOCs such as benzene and toluene could co-oxidize

with  $\text{CH}_4$ , other NMOCs including perchloroethylene, chlorofluorocarbon (CFC) 11 and CFC 12 do not degrade under oxic conditions and so their fate and transport is not directly influenced by  $\text{CH}_4$  oxidation in landfill covers (Kromman et al., 1998; Scheutz et al., 2004). Thus, when sufficient  $\text{CH}_4$  oxidation occurs such that  $\text{CH}_4$  emission rate is negative or zero, NMOC emission rate estimates are often underestimated  $\geq 10\times$ .

### 3.2.2. Measured versus predicted composite NMOC fluxes

USEPA operational standards described in 40 CFR 60.753 (USEPA, 1996) require estimation of composite NMOC flux using Eq. (1), where  $C_{\text{NMOC}}$  is expressed as an equivalent hexane concentration. Following USEPA guidance in 40 CFR 60.755 (USEPA, 1996), composite NMOC fluxes were computed from the field data, first expressing  $C_{\text{NMOC}}$  in g carbon for each species, summing over all species, and then dividing by six to estimate  $C_{\text{NMOC}}$  as hexane-C. Fig. 5 illustrates the effect of landfill cover type and thickness in predicted composite NMOC flux using the ratio method for landfill surfaces with positive  $\text{CH}_4$  emission rates. In this figure, only positive speciated measured NMOC fluxes are used. In terms of composite NMOC flux, for thick soil or biocovers ( $\geq 40$  cm) with positive  $\text{CH}_4$  flux, 82% of ratio method estimates exceed measured NMOC flux  $\geq 10\times$ . Note that one data point for thick biocovers does not appear in Fig. 5 because the measured NMOC flux is practically zero (i.e. speciated NMOC fluxes have zero or negative values) but its predicted NMOC flux is  $4.8 \times 10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$  hexane-C. For thin covers ( $<40$  cm, soil or biocover), though, predicted composite NMOC fluxes using the ratio method are in reasonable agreement with measured fluxes, with 87% of predictions within  $10\times$  of measurements.

### 3.2.3. Spatial variation in NMOCs/methane concentration ratios

The ratio method of estimating NMOC flux (Eq. (2)) assumes that the concentrations of individual NMOCs relative to  $\text{CH}_4$  in the gas well (or vent pipe) are representative of their concentrations in LFG that escapes into the atmosphere. In thick cover data sets where the ratio method overestimated the measured individual NMOC flux at the landfill surface (Table 3 and Fig. S3), speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios at the landfill surfaces were initially postulated to be lower than speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the gas well (or vent pipe) – which would explain the overestimation of NMOCs fluxes from the landfill surface. However, measured  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios at the landfill surfaces are generally higher than those of the gas well in the literature data sets analyzed here, which is consistent with data from 2012/2013 field campaigns discussed earlier. This is illustrated with data from soil covers for Lapouyade (Scheutz et al., 2003), Grand'Landes (Scheutz et al., 2008), and Leon County (Chanton, 2013) landfills (Fig. S4); select data from Grand'Landes and Leon County landfills are also shown in Fig. 6. For these data, 58–96% of NMOCs have higher  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios at landfill surface than in gas well (or vent pipe) in both thick (Scheutz et al., 2008) and thin (Chanton, 2013) soil covers. Thick soil covers tend to have more NMOCs (27–73%) that have concentration ratios  $\geq 10\times$  higher at the landfill surface compared to thin covers (17–29%) (Fig. S4).

The generally higher  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios at the landfill surfaces can be attributed to the 23–48%  $\text{CH}_4$  oxidation (mean range of four data sets, Table 2) measured at these sites. This may have caused the 5–6 order of magnitude difference in  $\text{CH}_4$  concentration reduction relative to NMOC concentration change between header gas and landfill surface measurements.

For biocovers the results are mixed (Fig. S5): landfill surface concentrations from Leon County landfill 30-cm thick biocovers (Chanton, 2013) have 44–75%  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios within  $10\times$  of vent pipe measurements, but 90–100% of the Outer Loop landfill data from 130-cm thick biocovers (Barlaz et al., 2004) have  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios within  $10\times$  of vent pipe measurements.

**Table 3**

Efficacy of USEPA model for speciated NMOC flux estimation.

LF Cover Systems			Landfill Site <sup>a</sup>	No. of Locations Tested <sup>b</sup>	CH4 flux (gm <sup>-2</sup> d <sup>-1</sup> )		No. of NMOCs Detected	% of NMOC Data with (-) or 0 flux		% NMOC Flux Data		
Type	Thickness cm	Components			Range	Mean		Range	Mean	Overestimated by ≥ 10x	Within 10x	Underestimated by ≥ 10x
Soil												
	100 -120	clay soil or clay/loam + sand	GL, LP	5	3.2E-1 to 29.0	13	35-45	24-88	47	78 ± 6 <sup>c</sup>	20 ± 5	2 ± 3
	100 -120	clay soil or clay/loam + sand	GL, LP	2	8.4E-3 to 1.0E-4	4.3E-3	35-45	60-69	64	30 ± 42	34 ± 48	36 ± 6
	100 -120	clay soil or clay/loam + sand	GL, LP	6	-9.5E-4 to 0	-3.0E-2	35-45	27-85	50	0	50 ± 28	50 ± 28
	40	coarse sand	LP	1		49.9	35		26	49	51	0
	15	clay soil	LC	8	1.9 to 165.9	57.0	53	4-15	9	20 ± 5	70 ± 4	11 ± 6
Biocovers												
	130	100 cm compost + 15 cm tire chips + 15 cm clay soil	OL	3	2.0E-2 to 9.2	5.9	40	98-100	98	98 ± 1	2 ± 1	0
	130	100 cm compost + 15 cm tire chips + 15 cm clay soil	OL	4	-8.0E-2 to -1.4E-1	-1.2E-1	40	20-98	74	0	74 ± 36	26 ± 36
	30	15 cm mulch + 15 cm clay soil	LC	7	2.2E-2 to 5.6	2.0	52-53	19-38	26	30 ± 9	37 ± 22	33 ± 20
	30	15 cm mulch + 15 cm clay soil	LC	1		-2.5E-1	53		36	0	36	64

<sup>a</sup> GL (Grand'Landes Landfill, France); LP (Lapouyade Landfill, France), OL (Outer Loop Landfill, KY, USA), LC (Leon County Landfill, FL, USA).<sup>b</sup> Static chamber tests for both CH<sub>4</sub> and NMOCs fluxes;<sup>c</sup> ±Values represent one standard deviation.

$C_{CH_4}$  ratios that are  $\geq 10\times$  lower compared to  $C_{NMOCs}/C_{CH_4}$  ratios in the gas well. For the Outer Loop landfill study, the lower  $C_{NMOCs}/C_{CH_4}$  ratios at the landfill surface compared to that of the header gas may be due to significant degradation of NMOCs in this data set, CH<sub>4</sub> generation within the biocover, and/or sub-optimal CH<sub>4</sub> oxidation. The tested biocover locations at Outer Loop landfill were found to have poor drainage and this most likely reduced CH<sub>4</sub> oxidation in biocovers (Barlaz et al., 2004). Furthermore, Barlaz et al. (2004) noted isotopic evidence that emitted CH<sub>4</sub> was generated from degrading organic matter from the biocover and not from landfilled wastes. The anaerobic decomposition in the biocovers could have contributed to the CH<sub>4</sub> concentration in the landfill surface air resulting in lower  $C_{NMOCs}/C_{CH_4}$  ratios than in gas well samples.

Plots depicting changes in gas concentrations and  $C_{NMOCs}/C_{CH_4}$  ratios of selected speciated NMOCs with soil depth for the data sets reviewed are provided in the SI (Figs. S6–S14). In general, when NMOCs like BTEXs biodegrade along with CH<sub>4</sub> in landfill covers, the  $C_{NMOCs}/C_{CH_4}$  ratios for these compounds did not change significantly in the soil profile. Some NMOCs including chlorinated ethylenes (e.g., trichloroethylene, tetrachloroethylene) and chlorinated methanes (e.g., chloroform, carbon tetrachloride, halo-carbons) are not degraded as much as CH<sub>4</sub> in landfill covers so their speciated  $C_{NMOCs}/C_{CH_4}$  ratios tend to increase near the landfill surface (0–20 cm).

### 3.3. Effect of cover thickness

Analysis of the literature data presented above indicates that the ratio method works reasonably well predicting NMOC emissions for landfills with thin soil or biocovers (<40 cm), but results in overestimation of NMOC emissions for thick covers ( $\geq 40$  cm) (Table 3 and Fig. 5). The only situations where this is not true are if the CH<sub>4</sub> flux is negative or near zero.

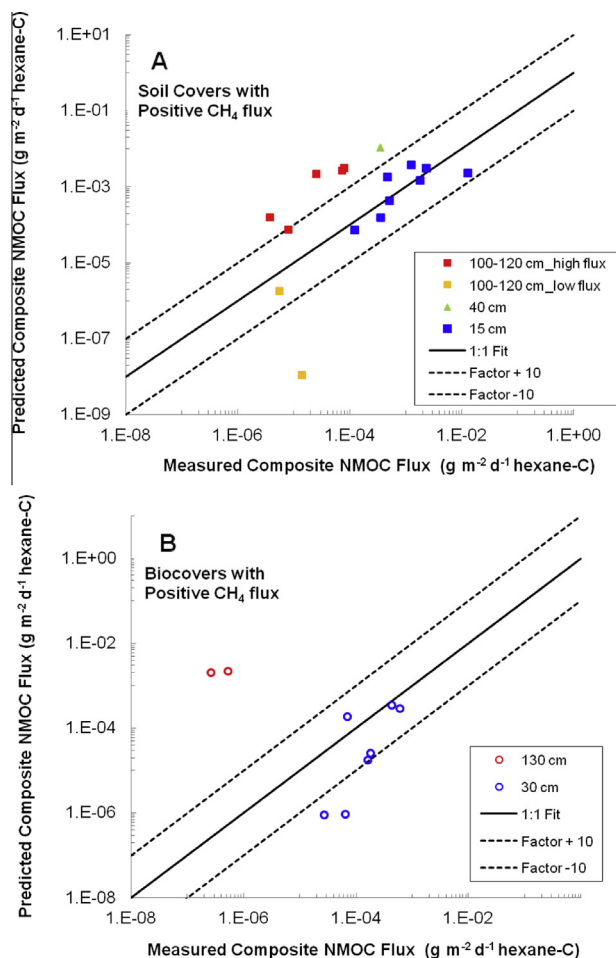
Cover thickness plays an important role in transport and reactions especially when gas diffusion is the dominant transport mechanism in the landfill cover system. The reason is that gas

concentration gradients ( $\frac{\partial C}{\partial z}$ ) that drive diffusion are a function of cover thickness. For example, if we assume fixed  $C_{CH_4}$  at the atmosphere (top) and landfill (bottom) boundaries of the cover, then  $\frac{\partial C_{CH_4}}{\partial z} \propto \frac{1}{\text{cover thickness}}$ . Thus, thicker covers result in smaller concentration gradients and smaller diffusive fluxes,  $J_{CH_4} \propto \frac{\partial C_{CH_4}}{\partial z}$ . Since residence time in a landfill cover  $\propto \frac{\text{cover thickness}}{J_{CH_4}}$ , residence time in the landfill cover  $\propto (\text{cover thickness})^2$ . Thus, thicker covers result in longer residence times, allowing more time for biological and chemical reactions. A similar analysis conducted for advective transport would yield a similar result – if gas pressure boundary conditions on thick and thin covers were similar. Unfortunately, this assumption could not be tested, since gas pressure data at the bottom of landfill covers were not available from the field and literature studies.

The ratio method may not work in landfills with thick covers because there is sufficient time for additional reactions to modify concentrations and fluxes of CH<sub>4</sub> and NMOCs. Supporting data for this hypothesis come from  $C_{NMOCs}/C_{CH_4}$  ratios. The ratios of NMOCs to CH<sub>4</sub> concentrations are plotted in Figs. 6 and S4 for thick and thin soil covers, and in Fig. S5 for thick and thin biocovers. When soil covers are thick ( $\geq 40$  cm),  $C_{NMOCs}/C_{CH_4}$  ratios are systematically larger at the top of the soil than in the nearby gas well or vent pipes. These thick covers provided sufficient residence time for biological and chemical reactions to alter concentrations. However, for thin soil covers (<40 cm), the bias disappears, and concentration ratios at the top of the soil are generally within a factor of 10 of nearby gas well or vent pipes. The situation is more complex with biocovers, though. For thin biocovers (<40 cm), just as with soil covers concentration ratios at the top of the biocover are generally within a factor of 10 of nearby well or vent pipes. However, for thick covers ( $\geq 40$  cm)  $C_{NMOCs}/C_{CH_4}$  are often smaller than concentrations in nearby well or vent pipes by greater than a factor of 10. Here, the additional residence time in these biocovers may have allowed CH<sub>4</sub> generation from degrading organic matter, or NMOC degradation.

In light of analyses of the literature data, it is worth considering the field data collected in 2012/2013. Three of the four field sites

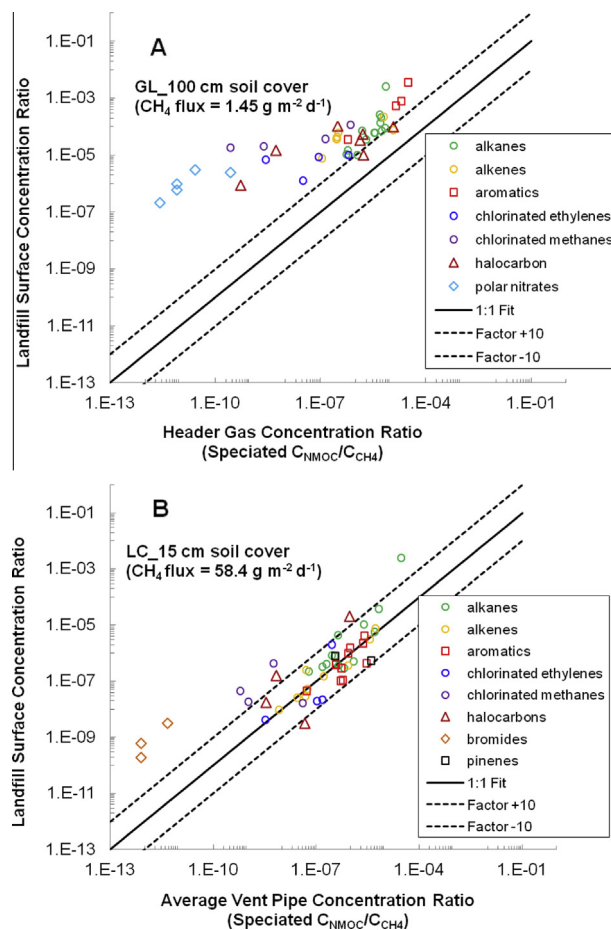




**Fig. 5.** Comparison of predicted composite NMOC flux in (A) soil covers and (B) biocovers with positive  $\text{CH}_4$  flux using the ratio method (Eq. (2)). Data points represent composite NMOC flux of tested landfill surface point locations from landfills listed in Table 3. High flux and low flux data points have  $\text{CH}_4$  fluxes ranging from  $29$  to  $10^{-1}$  and  $10^{-3}$  to  $10^{-4}$   $\text{g m}^{-2} \text{d}^{-1}$ , respectively. Solid black line indicates perfect model prediction, while dashed lines represent model predictions that are either greater than measured by a factor of 10 (upper line), or less than measured by a factor of 10 (lower line).

sampled had intermediate soil covers  $<40$  cm (see Table 1). Thus, we expect  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios to remain unchanged with sampling depth for Southeastern-US, Midwestern-US 1, and Midwestern-US 2 landfills. However, this was clearly not the case for Southeastern-US and Midwestern-US 1 landfills, as shown in Fig. 1. Here,  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios were higher at the soil cover surface than for samples with depth, which is consistent with behavior observed for thick landfill cover soils in the literature. In the very wet soil for Midwestern-US 2 landfill, though,  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios were not significantly altered with depth (Fig. 2B), consistent with the analysis of literature data for thin covers. Yolo County landfill was the single field site with a thick landfill soil cover (50–60 cm), and here  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios increased at shallower depths (Fig. 2A), consistent with literature data for thick covers. The 2012/2013 field data suggest that while significant chemical and biological reactions may be expected to alter  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios for thick covers, for thin covers results may vary and may be associated with other site-specific conditions. Thus, while the ratio methodology provided reasonable predictions of NMOC fluxes for the Leon County landfill with a thin soil cover, the same result may not be expected at other sites with similar thin landfill covers.

Finally, while the systematically higher speciated  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios at the landfill surface than in the nearby gas well or vent



**Fig. 6.** Examples of speciated concentration ratios of  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  in gas well/vent pipe and landfill surfaces with (A) thick (GrandLandes) and (B) thin (Leon County) soil covers. Data points represent individual NMOCs that were classified as alkanes, alkenes, etc.

pipe in thick covers could be plausibly attributed to ample residence time for additional reaction processes, the observed lower speciated NMOC flux relative to  $\text{CH}_4$  flux ( $Q_{\text{NMOC}}/Q_{\text{CH}_4}$ ), hence over-estimation of the NMOC flux by the ratio method, is not expected. This paradoxical observation is a phenomenon requiring further investigation.

### 3.4. Modifications to ratio method

Several modifications of the ratio method (Eq. (2)) using formulations that scale emissions with other chemical properties were used to explore more appropriate models to estimate NMOC emission rates from landfills with thick covers. The data set from the GrandLandes landfill study (Scheutz et al., 2008) was selected for model exploration because it had the largest number of low and high  $\text{CH}_4$  emission data collected for the same sampling period and landfill cover type (Table 2). Table 4 summarizes the performance of each model using mean data set values, i.e., average speciated NMOCs and  $\text{CH}_4$  fluxes for low and high  $\text{CH}_4$  emission locations.

Fig. 7A shows that NMOC flux estimates using Eq. (2) (Table 4, model 1) are higher than measured fluxes of most NMOCs (60%) by  $\geq 10\times$ . Note that since Fig. 7A is on a log scale, only positive measured speciated NMOC fluxes are shown; hence, plotted data points are fewer than 35–53 detected NMOCs (Table 3). The ratio method was first modified by incorporating Henry's Law constant,  $k_H$  (Table 4, model 3) since this parameter describes the air–water partitioning of organic compounds. NMOCs with higher  $k_H$  (more

volatile) will be more likely present in the landfill gas than in the leachate or aqueous solution, and thus, will most likely contribute to overall NMOC emissions. By replacing the MW ratio with Henry's Law constant ratio ( $k_{H,NMOC}/k_{H,methane}$ ), the  $k_H$ -modified Eq. (2) (Table 4, model 3a) resulted in NMOC flux estimates closer to the measured NMOC fluxes – only 16% of estimates are  $\geq 10\times$  (Fig. S15A). Emission rates of NMOCs that have low  $k_H$  ( $<10^{-4}$ ) such as ethyl nitrate (polar nitrates) are well underestimated by model 3a, though (Fig. S15A). Flux estimates for chlorinated methanes (such as tetrachloromethane (TeCM) and trichloromethane (TCM)), though relatively volatile ( $k_H = 10^{-2} - 10^{-3}$ ), are also underestimated by  $\geq 10\times$  using model 3a. Perhaps the potential for dipolar interactions by chlorinated methanes due to having electronegative Cl atoms complicates their fate and transport behavior (Schwarzenbach et al., 2003).

Aqueous solubility ( $S_w$ ) is the maximum amount of a chemical that will dissolve in pure water at a specified temperature. Factors affecting the solubility of chemicals in water include the solute's polarity and molecular size, ionic strength (presence of salts), temperature and pressure. Chemicals that have the potential to donate and/or accept electrons typically have molecular structures with O–H,  $-NH_2$ ,  $-COC$ ,  $C=O$ , or  $-COOH$  and are classified as polar compounds. These compounds will favorably dissolve in polar solvents such as water. Larger molecules generally do not dissolve

well in water compared to smaller molecules because of the higher energy requirement to create cavities between water molecules (Schwarzenbach et al., 2003). NMOCs with higher  $S_w$  will likely be more present in the landfill leachate or aqueous solution than in landfill gas. 60% of the NMOC flux estimates using the  $S_w$ -modified Eq. (2) (Table 4, model 5c) are within a factor of  $10\times$  of measured NMOC fluxes. Like the  $k_H$ -modified Eq. (2) (model 3a),  $S_w$ -modified Eq. (2) (model 5c) underestimates TeCM and TCM fluxes. The alkanes that are overestimated by 2–3 orders of magnitude are the C7–C10 hydrocarbons using experimental  $S_w$  values (EPI Suite TM v. 4.1) (Fig. S15B).

Other considered model parameters include log octanol–water partition coefficient ( $\log K_{ow}$ ) and vapor pressure (VP). Log  $K_{ow}$  is linearly correlated with partition coefficient describing sorption to sorbent organic matter (OM) (Schwarzenbach and Westall, 1981). NMOCs that are more hydrophobic tend to have higher log  $K_{ow}$  and will likely sorb to sorbent OM. The association of hydrophobic NMOCs with sorbent OM retards their transport in landfills and reduces their availability for biological and chemical degradation (Saquing et al., 2012; Sanin et al., 2000; Reinhart et al., 1991). Vapor pressure is indicative of the intermolecular attractions in chemical substances. It is dependent on the molecular size (i.e., larger molecules have lower VP) and molecular structure (i.e., specific ability to undergo van der Waals and polar

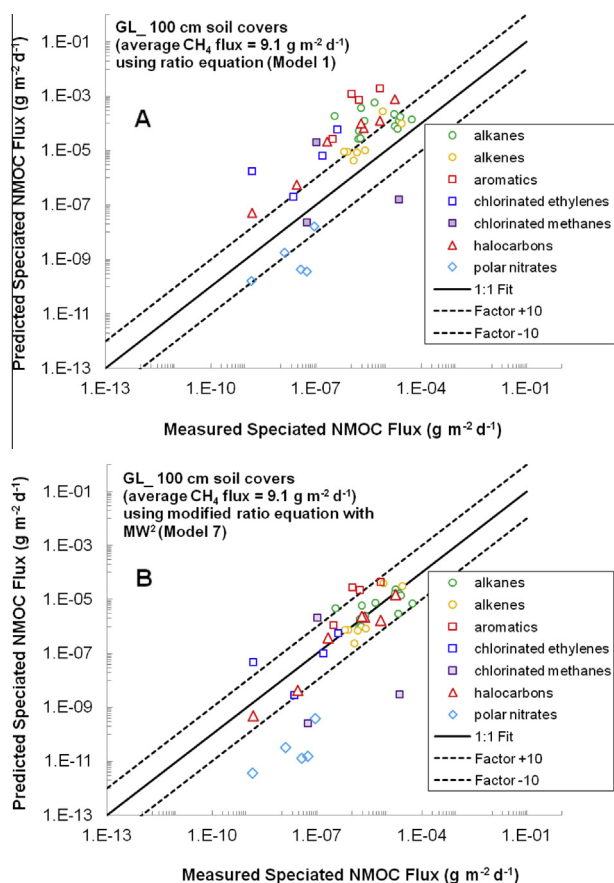
**Table 4**  
NMOC emission rates estimation models.

	Model	Model equation	Bias <sup>a</sup>	RMSE <sup>a</sup>	% Data overestimated by $\geq 10\times$	% Data underestimated by $\geq 10\times$	% Data within $10\times$
1	Ratio Eqtn	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})$	1.7E–4	3.9E–4	60	7	33
2	Ratio Eqtn with Conc ratio only	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})$	2.5E–5	6.0E–5	29	16	56
3a	Ratio Eqtn * $k_H$ ratio/MW ratio	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})(k_{H,NMOC}/k_{H,CH_4})/(MW_{NMOC}/MW_{CH_4})$	2.6E–5	8.9E–5	16	22	62
3b	Ratio Eqtn * $k_H$ ratio/MW ratio	Exclude NMOCs with very low $k_H$ ( $<10^{-4}$ )	3.0E–5	9.4E–5	18	13	70
4a	Ratio Eqtn * log $K_{ow}$ ratio/MW ratio	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})(\log K_{ow,NMOC} / \log K_{ow,CH_4})/(MW_{NMOC}/MW_{CH_4})$	7.6E–5	1.7E–4	42	13	45
4b	Ratio Eqtn * INV log $K_{ow}$ ratio/MW ratio	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{CH_4}/MW_{NMOC})/(\log K_{ow,NMOC} / \log K_{ow,CH_4})/(MW_{NMOC}/MW_{CH_4})$	–3.0E–6	1.2E–5	9	56	36
5b	Ratio Eqtn * INV $S_w$ ratio	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})/(S_{w,NMOC} / S_{w,CH_4})$	6.5E–3	3.7E–2	27	16	58
5c	Ratio Eqtn * INV $S_w$ ratio/(MW ratio)	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})/((S_{w,NMOC} / S_{w,CH_4}) / (MW_{NMOC}/MW_{CH_4}))$	7.5E–4	4.2E–3	13	27	60
6	Ratio Eqtn * VP ratio	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})(VP_{NMOC}/VP_{CH_4})$	–5.4E–6	1.1E–5	2	76	22
6a	Ratio Eqtn * VP ratio/MW ratio	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})(VP_{NMOC}/VP_{CH_4})/(MW_{NMOC}/MW_{CH_4})$	–5.8E–6	1.2E–5	2	84	13
7	Ratio Eqtn/(MW ratio) <sup>2</sup>	$Q_{NMOC} = Q_{CH_4} * (C_{NMOC}/C_{CH_4})(MW_{NMOC}/MW_{CH_4})/(MW_{NMOC}/MW_{CH_4})^2$	7.7E–7	1.2E–5	13	16	71
7a	Ratio Eqtn/(MW ratio) <sup>2</sup> – Apolar NMOCs	Exclude polar NMOCs	8.7E–7	1.3E–5	15	5	80
8	Two-parameter regression <sup>b</sup>	$Q_{NMOC}/Q_{CH_4} = 0.03(C_{NMOC}/C_{CH_4}) - 1.57(MW_{NMOC}/MW_{CH_4}) + 1.5E-6$	1.6E–7	1.0E–5	39	0	61
9	Three-parameter regression <sup>b</sup>	$Q_{NMOC}/Q_{CH_4} = 0.03(C_{NMOC}/C_{CH_4}) - 1.65(MW_{NMOC}/MW_{CH_4}) + 1.0E-7(k_{H,NMOC}/k_{H,CH_4}) + 1.4E-6$	2.6E–7	1.0E–5	37	2	61
10	Four-parameter regression <sup>b</sup>	$Q_{NMOC}/Q_{CH_4} = 0.03(C_{NMOC}/C_{CH_4}) - 1.7E-7(MW_{NMOC}/MW_{CH_4}) + 8.4E-8(k_{H,NMOC}/k_{H,CH_4}) - 5.5E-10((S_{w,NMOC}/S_{w,CH_4}) + 1.5E-6$	2.2E–7	1.0E–5	35	3	63
11	Five-parameter regression <sup>b</sup>	$Q_{NMOC}/Q_{CH_4} = 0.03(C_{NMOC}/C_{CH_4}) - 1.4E-7(MW_{NMOC}/MW_{CH_4}) + 1.6E-7(k_{H,NMOC}/k_{H,CH_4}) - 7.5E-10((S_{w,NMOC}/S_{w,CH_4}) - 1.9E-7(\log K_{ow,NMOC} / \log K_{ow,CH_4}) + 1.7E-6$	2.4E–7	1.0E–5	35	3	63
12	Three-parameter log regression <sup>c</sup>	$\log(Q_{NMOC}/Q_{CH_4}) = -0.9\log(C_{NMOC}/C_{CH_4}) - 1.95\log(MW_{NMOC}/MW_{CH_4}) + 3.19\log(k_{H,NMOC}/k_{H,CH_4}) - 10.86$	3.8E–6	2.5E–5	25	53	23

<sup>a</sup> Bias is the arithmetic mean of the errors and RMSE is root mean squared error. Equations and explanation for bias and RMSE are provided in the SI.

<sup>b</sup> Regression model is significant ( $p < 0.05$ ) but only the MW ratio is a significant contributing factor.

<sup>c</sup> Regression model is not significant ( $p > 0.05$ ).



**Fig. 7.** Predicted average flux of speciated NMOCs including three hot spots in Grand'Landes region 25A from Scheutz et al. (2008) using (A) model 1 (Eq. (2)) and (B) model 7 (Eq. (2) with inverse  $MW^2$ ). Data points represent flux of individual NMOCs. Solid black line indicates perfect model prediction, while dashed lines represent model predictions that are either greater than measured by a factor of 10 (upper line), or less than measured by a factor of 10 (lower line).

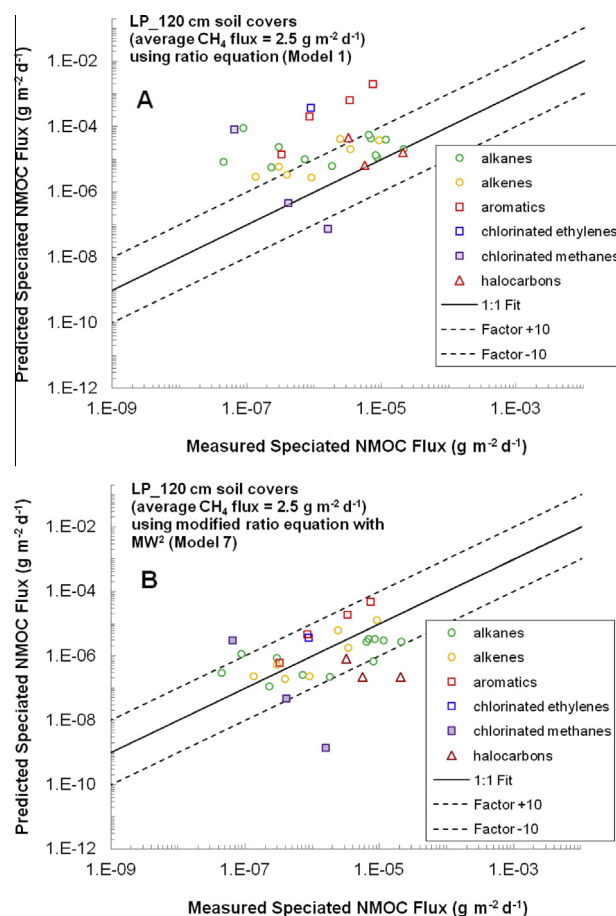
interactions). NMOCs that exhibit high VP at a given temperature do not have strong intermolecular attractions, and thus are likely to evaporate. As shown in Table 4, log  $K_{ow}$ -modified Eq. (2) (model 4a) overestimated 42% of NMOC fluxes by  $\geq 10\times$ , while VP-modified Eq. (2) (model 6a) underestimated 84% of NMOC fluxes by  $\geq 10\times$ . Compared to  $k_H$  and  $S_w$ , these parameters did not provide better estimation models for NMOC fluxes (Table 4).

Fig. 7B shows that  $MW^2$ -modified Eq. (2) (model 7) yields NMOC flux estimates that are closest to measured NMOC fluxes: 71% of estimated NMOC fluxes are within  $10\times$ , while 13% are overestimated by  $\geq 10\times$  (Table 4b). When simplified, model 7 is essentially Eq. (2) with an inverse  $MW$  ratio, i.e.,  $MW_{CH_4}/MW_{NMOC}$ . The improved predictions with model 7 suggest that NMOCs with higher  $MW$  (and thus smaller  $MW_{CH_4}/MW_{NMOC}$  ratio) likely remain in the solid and aqueous phases so their concentrations in emitted landfill gas will be lower (i.e.,  $C_{NMOCs}/C_{CH_4}$  ratio). Molecular weight describes the size of a chemical compound. Chemicals with higher  $MW$  generally have lower  $k_H$ ,  $S_w$  and VP but higher log  $K_{ow}$ . Larger chemicals are generally more difficult to biodegrade than smaller molecules because they likely sorb to surrounding organic matter and become inaccessible to microbial degradation in the aqueous solutions (Shaw et al., 2000; Harms and Zehnder, 1995). Moreover, larger chemicals in the aqueous phase may not be readily available for microbial degradation due to slower or restricted transport into the cell membranes (Boethling et al., 2007). The biodegradability of larger chemicals can be enhanced by longer residence times,

allowing more time for desorption from solid phases and transport in aqueous phases for biological and chemical reactions.

NMOC flux relationships involving two or more individual chemical properties were also explored through regression analysis (Table 4, models 8–12). Except for the log-transformed model (Table 4, model 12), all regression correlations are significant ( $p < 0.05$ ) with  $MW_{CH_4}/MW_{NMOC}$  ratio the only significant contributing factor. Moreover, regression coefficients for  $MW_{CH_4}/MW_{NMOC}$  ratio have negative values suggesting an inverse relationship between flux ratio ( $Q_{NMOC}/Q_{CH_4}$ ) and concentration ratio. Similar inverse relationships between concentration ratios and  $MW$  ratios were also observed in field data obtained from Southeastern-US (Fig. 1A), Midwestern-US 1 (Fig. 1B) Yolo County (Fig. 2A) and Midwestern-US 2 (Fig. 2B) landfills.

Among the alternative models,  $MW^2$ -modified equation 2 (ratio equation divided by  $MW^2$ , model 7) is best in addressing the tendency of the ratio method to overestimate NMOC flux estimates for thick covers. Application of this alternative model to Grand'Landes landfill data set reduced the speciated NMOC flux data overestimated by a factor  $\geq 10\times$  from 60% to 13%, and improved the speciated NMOC flux data that are within  $10\times$  factor from 33% to 71%. Similar results were obtained for Lapouyade landfill data set (Fig. 8): speciated NMOC fluxes overestimated by a factor  $\geq 10\times$  are reduced from 57% to 20% and the speciated NMOC flux data that are within  $10\times$  improved from 40% to 69% when model 7 is employed rather than the ratio method.



**Fig. 8.** Predicted average flux of speciated NMOCs in Lapouyade landfill from Scheutz et al. (2003) using (A) model 1 (Eq. (2)) and (B) model 7 (Eq. (2) with inverse  $MW^2$ ). Data points represent flux of individual NMOCs. Solid black line indicates perfect model prediction, while dashed lines represent model predictions that are either greater than measured by a factor of 10 (upper line), or less than measured by a factor of 10 (lower line).



#### 4. Conclusions

The current ratio method used in a recent USEPA Report (USEPA, 2012) uses  $\text{CH}_4$  flux measurements and measured  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios from landfill header gas to estimate speciated NMOC fluxes from the landfill. Header gas concentrations are in essence a composite gas sample of the landfill but may be significantly different from those gases in the cover soils, at the landfill surfaces, and downwind of the landfill as both NMOCs and  $\text{CH}_4$  are affected by processes in the landfill cover.  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios near landfill surfaces are generally higher than the  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios in the header gas. Both literature data and 2012/2013 field sampling data from US landfills show systematic vertical variation of  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  with higher concentration ratios observed in gas samples obtained at shallower depths. One explanation for this is that  $\text{CH}_4$  undergoes preferential biodegradation. An exception is noted for Midwestern-US 2 data, possibly due to excess moisture in pores due to prior rainfall before field sampling, this reducing  $\text{CH}_4$  biodegradation. Moreover, field pore gas data at 1.5 m depth and thus in the waste mass show no systematic horizontal variation in  $C_{\text{NMOCs}}/C_{\text{CH}_4}$  ratios ( $p < 0.05$ ) relative to the adjacent gas well, suggesting that off-gassing of some NMOCs due to vapor/vacuum interactions in the gas extraction process do not result in increased NMOC concentrations in the gas well.

The ratio method worked well predicting NMOC emissions for the single landfill site with thin covers (<40 cm) and no gas collection. This scenario would result in the least opportunity for  $\text{CH}_4$  biodegradation. However, ratio method results in overestimation of NMOC emissions for thick covers ( $\geq 40$  cm). The only situation where this is not true is when the  $\text{CH}_4$  flux is negative or near zero. Among the explored alternative models incorporating other chemical properties (Henry Law's constant, aqueous solubility, log octanol–water partition coefficient, vapor pressure, and molecular weight (MW)) into the ratio method,  $\text{MW}^2$ -modified ratio equation (ratio equation divided by  $\text{MW}^2$ , model 7) was best in addressing the tendency of the ratio method to overestimate NMOC fluxes for thick covers. Application of this alternative model to Grand'Landes and Lapouyade landfill data improved the percentage of speciated NMOC flux data estimates within  $10\times$  of actual measurements. Future work should examine the utility of the ratio method for whole-landfill NMOC emissions when such data are available.

#### Acknowledgments

We thank Waste Management, Inc. for their financial support of this work and field sampling assistance from Terry Johnson and Tom Pike. Roger B. Green and Gary R. Hater from Waste Management, Inc. also provided technical suggestions on various aspects of this research and are gratefully acknowledged.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.wasman.2014.07.007>.

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